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Abstract

Full Text

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## CHEMISTRY

A. I. TITOV, P. O. GITEL

## ON THE REACTION OF WHITE PHOSPHORUS WITH ALKYL HALIDES BY IONIC AND RADICAL MECHANISMS

*(Presented by Academician M. M. Shemyakin on 12 V 1964)*

The simplest and most elegant method for obtaining organometallic compounds is the reaction of active metals with halogen derivatives  $RX$ . White phosphorus, as is evident from its ability to displace Cu and Pb from aqueous solutions of their salts, approaches metals of this kind, and therefore it may be called a pseudometal. By donating electrons to  $R-X$ , phosphorus could cause the appearance of free radicals. On the other hand, in the tetrahedral molecule  $:P_4$  the presence of lone electron pairs should be manifested. The "basic" properties of  $:P_4$  should be expressed more strongly than in  $:PCl_3$ , and probably more weakly than in  $:PH_3$  and  $:PR_3$ , since, according to B. V. Nekrasov (<sup>1</sup>), the relative electronegativities of H, P, and C in typical compounds (1; 1.13; 1.19) are close; this is confirmed by the identical electronegativity values of H and P according to Pauling (2.2) and by the small dipole moment of  $PH_3$  (0.55 D). Not only  $:PH_3$ , but even  $:PCl_3$ , is capable of adding  $R-X$ , more readily in the presence of  $AlCl_3$ , i.e., undoubtedly by the ionic type in the form  $R^+AlCl_4^-$  or a form close to it (<sup>2</sup>). This gave grounds to expect a comparatively easy addition to  $:P_4$  of active alkylating agents  $RX$  by an ionic mechanism, which is more promising for synthetic purposes.

The radical pathway of the reaction was most probable for halogen derivatives of the type  $Cl_3\overset{\downarrow}{C}-Br$ . Indeed, trichlorobromomethane reacted rapidly with  $P_4$  upon heating below the boiling point. However, the principal solidifying fraction of the reaction mass, with b.p. 90-110° at 17 mm, consisted mainly of  $Cl_3C-CCl_3$ , the dimerization product of the trichloromethyl radical  $Cl_3C\cdot$ .

The reaction by the ionic mechanism, as we suppose, predominated under the action of alkyl halides of the type  $C_6H_5\overset{+\delta}{C}H_2-Br$ . Thus, upon heating to 150° for

1.5 hours, 97 g of  $C_6H_5CH_2Br$  with 10 g of P in a stream of  $CO_2$ , all the phosphorus entered into the reaction, with evolution of HBr being observed. After 6 hours of holding below the boiling point, the mixture was distilled in vacuum. The following fractions were isolated: I, toluene with b.p.  $110^\circ$  and  $n_D^{15}$  1.499, about 5 g; II,  $PBr_3$ , with b.p.  $169-172^\circ$ , about 6 g; III, benzyldibromophosphine, with b.p.  $142-143^\circ$  at 10 mm, 27 g ( $\sim 30\%$  based on P)—a colorless fuming liquid.

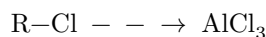
Found, %:  $P$  10.8;  $Br$  57.2.  
 $C_7H_7Br_2P$ . Calculated, %:  $P$  11.0;  $Br$  56.7.

Upon crystallization of the residue from the distillations from aqueous alcohol, about 30 g of bromide of tetrabenzylphosphonium was obtained, with m.p.  $215-216^\circ$  ( $\sim 45\%$  based on  $C_6H_5CH_2Br$  and  $20\%$  based on P).

Found, %:  $P$  6.4;  $Br$  16.2;  $C$  70.1;  $H$  5.8  
 $C_{28}H_{28}BrP$ . Calculated, %:  $P$  6.5;  $Br$  16.8;  $C$  70.7;  $H$  5.9

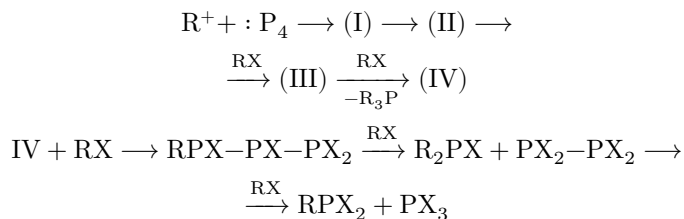
If, after carrying out the reaction, the mixture is diluted with  $CCl_4$ , filtered, and the phosphonium salt is washed with  $CCl_4$ , then by fractionation of the solution one can obtain a signi-

considerably larger amounts of benzyldibromophosphine, with some decrease in the yield of  $(C_6H_5CH_2)_4PBr$ .  $CH_3I$  entered completely into reaction with P in 4 h at  $100^\circ$ , while  $C_6H_5CH_2I$  reacted many times faster. Thus, the use of active bromides and iodides of alkyls in the reaction with P makes possible the convenient and rapid preparation of a number of organophosphorus compounds. The activity of R-Cl can probably be increased by adding suitable acids ( $AlCl_3$ , etc.), which greatly increase the polarization

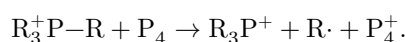


up to the formation of  $R^+$ .

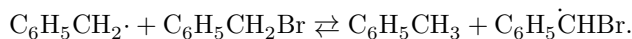
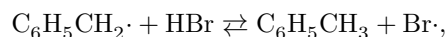
The ionic mechanism of the reaction of R-X and  $:P_4$  may be represented as follows:



The addition of  $R^+$ , free or at the moment of reaction of  $R-X$ , to the lone pair of electrons of  $:P_4$  gives the cation  $RP_4^+$  (see I). Polarization of the  $P-P$  bonds in I leads to addition of  $X^-$  and formation of  $RP_4X$  (see II). Continuation of this kind of process gives a mixture of  $R_3P$ ,  $R_2PX$ ,  $RPX_2$ , and  $PX_3$  (underlined in the scheme). Upon further reaction involving  $RX$ , a more or less equilibrium mixture of these compounds and  $R_4PX$  is formed. In the described case of the reaction of  $P$  with  $C_6H_5CH_2Br$ , the circumstances favored the formation of  $C_6H_5CH_2PBr_2$ ,  $(C_6H_5CH_2)_4P^+Br^-$ , and  $PBr_3$ . These compounds took part in the reaction, in particular  $R_4P^+X^-$  as a donor of  $R^+$  and  $X^-$ . Reacting with  $P_4$ , like  $Cu^{2+}$  and  $Pb^{2+}$ , they led to the formation of free alkyls:



The cations  $RPX_3^+$  and  $R_2PX_2^+$  acted on  $C_6H_5CH_2X$  as halogenating agents with formation of  $HX$ . The side formation of toluene probably occurred by radical mechanisms:



In the interaction of  $C_6H_5CH_2Cl$  with  $P$  in sealed tubes at  $300^\circ$ , when  $HCl$  remained in the reaction sphere and the high temperature favored radical processes, toluene became the main product <sup>(4)</sup>. Transformations of  $C_6H_5CH_2\cdot$  and  $C_6H_5\dot{C}HX$  could lead to the formation of a number of other compounds.

L. M. Smorgonskii took part in this investigation in 1951. In the cited article <sup>(4)</sup>, a review was given of other works on the reaction of  $P$  with halogen derivatives; its authors were also aware of the initial results of our investigation.

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6 V 1964

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2. J. P. Clay, *J. Org. Chem.*, **16**, 892 (1951).
3. A. N. Barashnikov, A. I. Titov, *DAN*, **91**, 1101 (1953).
4. K. A. Petrov, V. V. Smirnov, V. I. Emel' yanova, *ZhOKh*, **31**, 3027 (1961).

\* At the corners of the tetrahedron  $:P_4$  and of its adducts there are atoms  $:P$  with lone pairs of electrons. It is necessary, however, to take into account the

bent,  $\pi$ -like character of the P–P bonds in three-membered rings. Therefore addition of  $R^+$  in the initial phase may also proceed by the mechanism accepted for cyclopropane (<sup>3</sup>). Addition of R–X, as such, may occur through use of the *d*-orbitals of phosphorus for bonding with X.

*Note: Figure translations are in progress. See original paper for figures.*

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